ORIGINAL PAPER

Dispersion of contaminants from a lead processing industry in a toposequence dominated by vertisol

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Abstract

In 1997, 500,000 MG of mine tailing materials containing 3% lead (Pb), 21% cadmium (Cd), and 13% zinc (Zn) were buried at a site in Santo Amaro, Bahia, Brazil. The present study evaluated the dispersion of contaminants in a toposequence classified by the FAO system: Pellic Vertisol (hilltop, P1), Leptic Vertisol (upper third of the slope, P2), Leptic Endospolic Technosol (middle third, P3), Haplic Vertisol (lower third, P4), and Eutric Fluvisol (footslope, P5). The P1, P2, and P3 soil profiles were located within the processing plant boundary, whereas P4 and P5 were located outside the plant. According to the Brazilian Environmental Agency, the maximum concentrations of Pb and Cd were detected to be 26.4 and 2.6 times higher than the industrial intervention value, respectively, whereas Zn concentration was 1.9 times higher than the residential intervention limit. In the Technosol P3 region, the concentrations of Pb and Cd were above or around the industrial value, whereas Zn concentration ranged from agricultural to industrial values. The metal concentration in the Fluvisol (P5) region was lowest among all soil profiles; however, the concentration of Pb remained above the agricultural intervention limit. The high concentrations of metals, especially Pb, in the P4 and P5 regions are an evidence that after almost two decades, the contaminants still continue to sediment from the top to the lowland area of the toposequence.

Keywords Pedogenesis · Soil classification · Anthropic activities · Trace metal

Introduction

Brazil is a major player in the global mining industry. The state of Bahia is the fifth largest mining territory in Brazil (SDE 2016). In 1960, a lead alloy processing industry was established at the banks of the Subaé River in Santo Amaro, Bahia. The emission of particulates from the factory chimney and the overflow of waste from the containment basin to the Subaé riverbed caused one of the most emblematic cases of urban contamination in the World. The mine located in the city of Boquira, Bahia, approximately 606 km from Santo Amaro, was from 1956 to 1985, the main lead producer in Brazil. The ore extracted from rocks of the Boquira formation, consisting of chlorite-granite-biotite schists, quartzites, limestones, marbles, itabirite and amphibolites,

contained about 9% lead, 3% zinc and 32 grams silver per ton (Bertolino et al. 2014). The dominant sedimentary bands in the region host the stratabound and/or stratiform mineralization of the Pb–Zn (Cd–Ag) of the Boquira Formation and are closely associated with the subfacies BIF, silicate–magnetite (Silva and Cunha 2000). After 32 years of operation, the smelter produced and stocked approximately 500,000 MG mine tailing materials (20% to 25% SiO_2, 28% to 35% FeO, 15% to 20% CaO, 1% to 3% Pb, and 8% to 35% Zn). In 1997, the Public Ministry of the State of Bahia condemned the industry to encapsulate the mine tailing materials. In order to minimize the effects of contaminant materials during the rainy season, the Ministry took a palliative action, and the mine tailings were buried. The industry compromised to comply with the technical standards of the Brazilian legislation; however, the complementary measures were never implemented.

The harmful environmental impacts of metal accumulation in water and soil are still present in Santo Amaro (Fernandes et al. 2012; Bomfim et al. 2015). The current research was aimed at evaluating the effects of mine tailing materials on soils within and around the toposequence area.

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Materials and methods

Study area

The experimental study was carried out in the geographic micro-region of Santo Antônio de Jesus (IBGE 2014) in the municipality of Santo Amaro. The climate of the region is tropical humid with an average annual temperature of 25.4 °C (maximum 31 °C and minimum 21.9 °C) and an average annual rainfall of 1540 mm (SEI 2014). The geology of the area is formed by different rock structures: *Candeias* (shale and siltstone interspaced with limestone, dolostone, and sandstone), *Island* (shale and sandstone interspaced with marl, calcite sandstone, carbonaceous shale, siltstone, and calcilutite), *Sergi* (conglomeration of fine-grained sandstones and subordinate pelit besides *wetlands* and *mangroves deposits*) (BRASIL 1999; CPRM 2012).

Sampling

The 728-m toposequence is located in the northwest urban area of the municipality of Santo Amaro, and the mine tailing was buried about 20 years ago. The sampling area was selected based on the regional and local reliefs, the characteristics of existing soils, the geological difference, and the presence of mining tailing (Fig. 1). Based on these criteria, five profiles were selected for sampling: Pellic Vertisol (hilltop P1), Leptic Vertisol (upper third of the slope P2), and Leptic Endospolic Technosol (middle third P3) were located inside the factory ground, whereas Haplic Vertisol (lower third P4) and Eutric Fluvisol (footslope P5) were located outside the plant property. The soil samples were collected from the horizons and different layers for morphological analysis (Santos et al. 2015) and stored in plastic bags, which were placed in a cold chamber at 4 °C for subsequent chemical and physical examination.

Soil sample analysis

The disturbed soil samples were air-dried, crumbled, and ground with a soil hammer mill (SOLAB SL 33) and passed through a 2-mm sieve to obtain air-dried soils.

The pipette method was adopted to evaluate the dispersion of clay in water and soil texture. Of the soil sample, 20 g was first dispersed in a solution of 100 mL water and 10 mL sodium hexametaphosphate $(NaPO_3)_6$ (1 mol L^{-1}). After overnight reaction, the mixture was shaken for 16 h at a speed of 30 rpm in a Wagner agitator (Model: TE–161). The coarse sand (CS), fine sand (FS) silt, and total clay fractions were determined (Donagema et al. 2011). The clay dispersion, a measure of aggregate stability and soil susceptibility to erosion, was calculated by the following equation:

Clay dispersion (%)

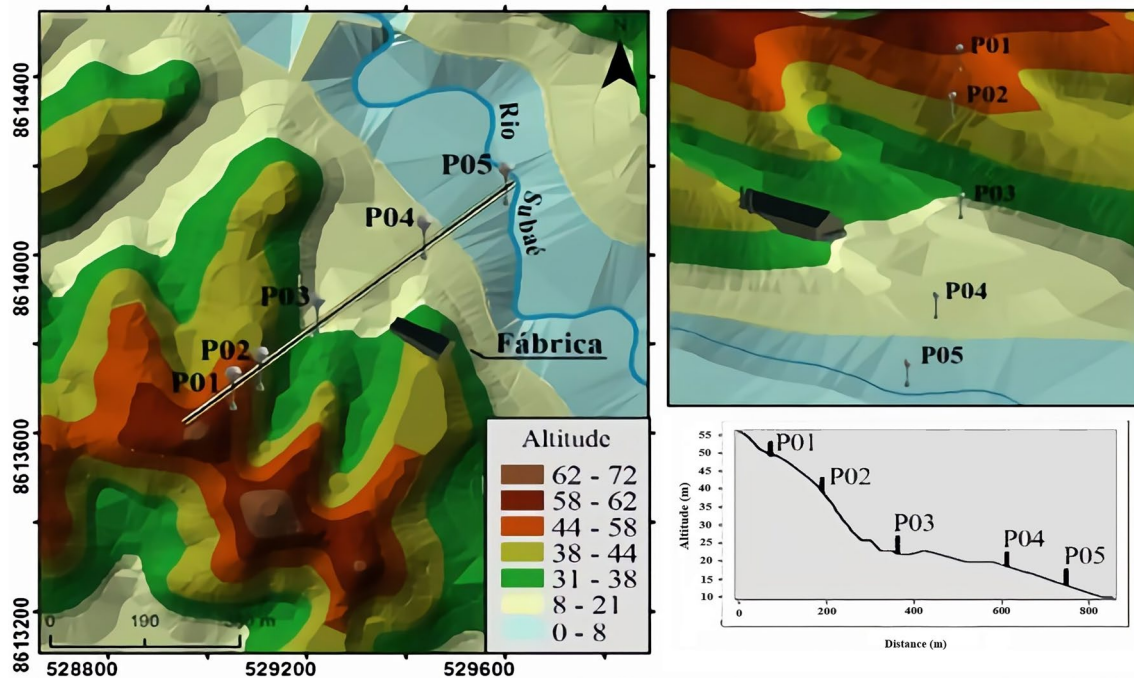$$= \frac{(100 - (\text{Total clay} - \text{clay dispersed in water}))}{\text{Total Clay}} \times 100$$

Fig. 1 Maps of the studied area on the banks of the Subaé River, Santo Amaro—Bahia

where total clay is the clay concentration in mol L^{-1} sodium hexametaphosphate solution and clay dispersed in water is the fraction of clay unstable in water suspension.

The samples were chemically characterized in a solution of water and 1 M KCl (soil/solution ratio of 1:2.5). Both exchangeable cations (Ca^{2+}, Mg^{2+}, and Al^{3+}) and potential acidity (H + Al) were determined by titration with 1 mol L^{-1} KCl and 0.5 mol L^{-1} calcium acetate (at pH of 7.0), respectively. The concentrations of exchangeable Na and K were analyzed by flame photometry, whereas the concentration of P was determined by photocolorimetry in the Mehlich–1 solution (Donagema et al. 2011). The organic C (C-org.) was determined according to the method proposed by Yeomans and Bremner (1988).

The trace metals Pb, Cd and Zn were evaluated in this study because the concentrations of Pb (25.000 ppm), Cd (63 ppm) and Zn (69.000 ppm) (Machado et al. 2012) in the slag were higher than the industrial intervention values recommended by the Brazilian Environmental Agency (CONAMA 2013), (Pb = 900 ppm; Cd = 20 ppm; and Zn = 2000 ppm). Pb, Cd, and Zn were extracted according to the 3050B method (USEPA 1996), and their concentrations were determined by an atomic absorption spectrophotometer (AAS model Varian AA 220 FS). Based on the data obtained, it was calculated: the sum of bases (S); cation exchange capacity (CEC); base saturation (V); and clay activity or T-clay (cmol$_c$ kg^{-1}) = (CTC pH 7,0/clay (%))×100).

Results and discussion

Morphologies and genesis of soils in the toposequence

It was found that from the hilltop to the lower third of the toposequence, the soils were formed by sedimentary rocks (shale), which experienced several vertisolization processes (indicated by the presence of nearly 1 cm wide cracks on rock surfaces). Table 1 depicts different structures of sedimentary rocks: wedge-shaped (P1 and P2), prismatic (P3 and P4), compression surface (P1 and P2), and friction (P4). The vertic properties of P1 and P2 were not clearly visible during the experiment because the samples were wet; however, they were easily observed in the dry soil samples collected in P4. The vertic characteristics were not detected in P5. The horizon and the layers of P5 were weakly developed and varied in colors due to the irregular presence of organic materials and minerals (Table 1). The characteristics of the parent materials (associated with humid weather) were the determining factors for the formation of vertic horizon (Biv) in P1, P2, and P4. The strong action of region climate factors (hot temperature and high humidity) on sedimentary clayey and silty rocks (shale intercalated with limestone and dolomite; CPRM 2012) was more dominant than the relief factors, which were classified as flat (P1) and smooth corrugated (P2 and P4).

The P1, P2, and P4 profiles represented the horizons A–Bi–C. The P3 and P5 profiles had the horizons A–C with the presence of corrugated and irregular transition. In P3, the horizon C was formed from the deposition of mine tailings and adjacent soil materials, while the horizon A was developed on the top of C-horizon by successive deposition of organic residue from brachiaria. The P5 profile was formed on the alluvial terrace with stratified layers by rainwater and meandering river, such as the Subaé River. It was noticed that the clay layer existed above the sandy alluvial layers, thus indicating the fluvic characteristics of colluvium and alluvial nature.

The P1 to P4 profiles were relatively young with a maximum depth of 100 cm above the rock fragments. The P5 profile was deeper (> 215 cm in depth) and presented stony layers composed of rounded quartz pebbles developed from quaternary deposits (Table 1). In P3, the middle third of the landscape had a smooth wavy relief and went through a process of soil formation due to the accumulation of technogenic materials (IUSS Working Group WRB 2015) or contaminants.

Physical characteristics of soils

The textures of P1, P2, and P4 profiles varied from clayey to very clayey, and the fine sand fractions were greater than the coarse sand in those profiles. A clay texture prevailed across all horizons and layers of P3 profile except the layer 3C, which was mainly composed of gravel materials from mine tailings (Table 2). The texture of the horizon of P5 ranged from sandy to sandy clay loam, which was composed of clayey soils, river sediment sand, and gravels.

The clay dispersion (> 63%) in the top 20 cm indicated that all soils of the toposequence were highly susceptible to erosion. The predominant wavy relief contributed to the increase in the transference of soil and sediments from the top to the lowland area of the toposequence.

Chemical characteristics of soils

The pH$_{H2O}$ of soils ranged from 4.9 (high acidity, P1-Biv) to 8.5 (high alkalinity, P3-C3) (Table 3). The low pH values signify that hot and humid weather strongly influenced the soil acidity regardless of the parental material characteristics. The P3 region manifested higher pH values, which were associated with the higher percentage of calcium saturation (> 72.9 in the first 78 cm), and consequently, lower exchangeable and potential acidity was observed in the horizon and layer of the profile.

Table 1 Morphological characteristics of soil profiles near the old lead processing factory, Santo Amaro—BA

Lay.	Depth (cm)	Wet color	Mottled	Sup. fric/ comp.	Structure	Consistency			Transition
						Dry	Moist	Wet	
Profile 1—typic orthic haplic vertisol, contaminated, moderately drained									
Ap1	0–5	GLEY1 2.5/N	–	–	BS, Mod, Mid and larg, mod, mid	–	Steady	m. plas and m.peg	Pla and cla
Ap2	5–15	7.5 YR 2.5/1	–	–	BS, Mod to for, gra,	–	Steady	m. plas and m.peg	Pla and grad
AB	15–39	7.5 YR 3/1	–	–	BS, mod, gra,	–	Friable	pla and peg	Pla and grad
BA	39–46/49	7.5 YR 4/3	–	–	BS, mod, gra,	–	Friable	m. plas and peg	Ond and cla
Biv	46/49–63/70	5YR 4/6	5Y 5/3	Common	BS, Mod, gra and cun	–	Friable	plas and m.peg	Ond and cla
C	63–85+		10YR 4/6; 5Y 5/3; 5Y 6/4	–	fra, BS, gra,	–	Steady	pla and peg	–
Profile 2—typic orthic haplic vertisol, contaminated, moderately drained									
Ap	0–7	10YR 3/2		–	BS, Mod, med and gra,	–	Friable to steady	m. plas and peg	Pla and grad
AB	7–20/37	–	5YR 4/3; 10YR 4/6; 5Y 6/3	–	BS, Mod, gra	–	Steady	m. plas and peg	Ond and cla
Biv	20/37–48/53	–		Common	Mod, BS, gra, cun	–	Friable to steady	m. plas and m.peg	Ond and grd
BC	48/53–50/57	–		–	maç,	–	Friable to steady	pla and peg	Irr and cla
Cr	50/57 +	–		–	cas,	–	Friable to steady	pla and peg	–
Profile 3—typic eutrophic regolithic neosol heavily contaminated anthropic									
Ap	0–5	5Y 5/4		–	BS, fra, med to gra,	–	Steady	m. plas and m.peg	Pla and cla
C1	5–35 (25–40)	2.5Y 4/4; 10 YR 4/6; 5Y 4/2	5Y 4/3	–	maç,	–	steady	m. plas and m.peg	Irr and cla
C2	35–78	10 YR 5/8; 5Y 4/2; GLEY 2 3/10B	5Y 5/2	–	maç,	–	Steady	m. plas and m.peg	Pla and grad
C3	78–100	GLEY 2 2.5/5 PB	–	–	maç,	Ext. hard	Extr. hard	–	–
Profile 4—gleysolic orthic haplic vertisol, heavily contaminated, imperfectly drained									
Apg	0–12	GLEY 2 4/5 PB	–	–	BS, mod, peq to med and gran, mod, peq to med	Hard	Steady	Plas and peg	Pla and abr
ABg	12–28	GLEY 2 5/5 PB	–	–	Pris, fort, gra and blang, med, mod	m.hard	Msteady	m. plas and peg	Pla and grad
BAg	28–40	GLEY 1 4/5G	7.5YR 5/8	–	Pris, fort, gra and blang, med, mod	m.hard	Msteady	m. plas and peg	Pla and grad
Bivg	40–71	10YR 4/6	GLEY 1 5/5G	Common	Pris, fra, m.gra and blang, fra, mgra	Very Hard	Msteady	m. plas and peg	Pla and dif

Table 1 (continued)

Lay.	Depth (cm)	Wet color	Mottled	Sup. fric/comp.	Structure	Consistency			Transition
						Dry	Moist	Wet	
Cvg	71–95	GLEY 1 6/5G	–	Common	Blang, fra, gra	Very hard	Msteady	m. plas and peg	
Profile 5—typic Ta eutrophic fluvic neosol, contaminated, well drained									
Ap	0–10	7.5 YR 3/3	–	–	BS, fra, med and maç	Hard	Friable to steady	Ligpla and ligpeg	Pla and clã
C	10–43 (34–39)	7.5 YR 4/3	–	–	BS, fra to mod, med	–	Friable to steady	Ligpla and peg	Irr and clã
2C	43–76 (72–80)	7.5 YR 4/3	–	–	BS, gra, fra, mod	–	Friable	Ligpla and n.peg	Ond and cla
3C	76–96 (90–107)	–	5YR 4/4; 5YR 3/1; 5YR 5/8	–	BS, med, gra, fra,	–	Friable	Ligpla and n.peg	Irr and clã
4C	96–132	–	5YR 3/1; 5YR 4/6; 7.5 YR 4/6; 7.5YR 6/4	–	BS, med to gra, fra, simple grains	–	Very friable	n.pla and n.peg	Pla and abr
5Cg	132–149	GLEY1 6/N	5YR 5/8	–	BS, fra, gra,	–	Friable to steady	m. plas and peg	Pla and abr
6C	149–166	5YR 4/6	5YR 6/1;	–	Simple grains	–	Loose	n.pla and n.peg	Pla and abr
7C	166–202	–	5YR 4/6; 5YR 3/4;—5YR 7/1; 5YR 4/3; 5YR 2.5/1	–	Simple grains	–	Loose	n.pla and n.peg	Pla and abr
8C	202–215+	10YR 7/1	10 YR 5/1	–	Simple grains	–	Loose	n.pla and n.peg	

arg, clay; arg.are, sandy clay; m.arg, very clayey; farg, clay loam; f.arg.are, sandy clay loam; BS, sub-angular grains blocks; maç, massive; cas, gravel; peq, small; med, medium; cun, wedge-shaped structure; mod, moderate; fra, weak; gran, granular; pmed, small and medium; fmod, weak to moderate

Moreover, all soils possessed constant charge because the delta pH values were lower than −0.5 and the clay activity was greater than 27cmol$_c$ kg^{-1} (Table 3) (Uehara and Gillman 1981). An analysis of the mineralogical characteristics of vertisols in the region of Santo Amaro, Embrapa (2000) indicated that illite and illite–smectite were the main minerals in the clay fraction.

The sum of base and CEC of P5 was lower than that of other profiles (Table 3). Despite the clay contents (7 g kg^{-1} to 37 g kg^{-1}) of layers 6C, 7C, and 8C, the clay activity (T-clay) on those layers ranged from 121 cmol$_c$ kg^{-1} to 153 cmol$_c$ kg^{-1}. The T-clay values in these layers were higher than that of other profiles. The criteria for the classification of T-clay were not applicable to layers 4C, 6C, 7C, and 8C because the soils of these regions were of sand and sand loam classes (Santos et al. 2013).

The chemical characteristics of first horizons and layers of P1, P2, and P3 were similar because of the susceptibility to erosion; however, the last layer of P3 was predominantly formed by mining tailings.

The exchangeable acidity (Al^{3+}) was classified as very high (> 2.0 cmol$_c$ dm^3) in the horizon Biv in P1 and in the layer Cvg of P4; low (0.21–0.50 cmol$_c$ dm–3) in P2; and very low (≤ 0.20 cmol$_c$ dm^3) in P3 and P5 (Ribeiro et al. 1999) (Table 3). The Al concentration was regarded as a minor factor because the percentage of base saturation was greater than 65%.

The concentrations of C-org in all soil profiles were low (≤ 0.4 dag kg^{-1}) and decreased with the increasing depths. The concentration of C-org on the horizon Ap1 (0.5 dag kg^{-1}) of P1 was an exception to the rule. The discontinuity in C-org concentration was attributed to the anthrosolization process (disposal of soil and mining tailing layers) in P3 and the fluvic character of colluvium-alluvial nature in P5.

Concentrations and distributions of trace metals

The input of trace metals in soils by anthropic processes significantly influences the environment of Santo Amaro

Table 2 Physical characteristics of the soil profiles sampled in toposequence that extends from the vicinity of the old lead factory to the banks of the Subaé River, Santo Amaro, Bahia

Horizons		Texture (g kg^{-1})				AD (g kg^{-1})	GD (%)	Textural class
Simb.	Depth (cm)	Sand		Silt	Clay			
		Coarse	Thin					
Profile 1								
Ap1	0–5	16	72	404	507	440	87	Clayey
Ap2	5–15	16	52	326	605	540	89	Very clayey
AB	15–39	18	53	295	632	560	89	Very clayey
BA	39–47 (46–49)	178	46	250	685	580	85	Very clayey
Biv	47–63 (56–70)	8	24	242	725	500	69	Very clayey
C	63–85+	6	23	308	662	540	82	Very clayey
Profile 2								
Ap	0–7	16	43	281	658	540	82	Very clayey
AB	7–28 (20–37)	4	29	279	687	610	89	Very clayey
Biv	28–48 (46–53)	5	18	323	652	560	86	Very clayey
BC	48–55 (53/57)	17	36	330	615	510	83	Very clayey
C	55 +	27	27	368	576	480	83	Clayey
Profile 3								
Ap	0–5	75	23	383	517	410	79	Clayey
C1	5–35 (25–40)	101	14	376	507	318	63	Clayey
2C	35–78	256	15	261	466	220	47	Clayey
*3C	78–100	–	–	–	–	–	–	–
Profile 4								
Apg	0–12	79	126	266	527	400	76	Clayey
ABvg	12–28	64	141	226	567	460	81	Clayey
BAvg	28–40	17	40	205	736	590	80	Very clayey
Bivg	40–71	8	22	158	810	570	70	Very clayey
Cvg	71–95	7	17	169	805	570	71	Very clayey
Profile 5								
A	0–10	265	400	73	261	180	69	Sandy clay loam
C	10–43 (34–39)	121	480	107	290	210	72	Sandy clay loam
2C	43–76 (72–80)	52	656	132	157	130	83	Sandy loam
3C	76–96 (90–107)	162	544	131	161	140	87	Sandy loam
4C	96–132	344	493	58	103	98	95	Sandy loam
5Cg	132–149	123	416	205	253	180	71	Sandy clay loam
6C	149–166	600	303	37	58	50	85	Sand
7C	166–202	890	47	19	42	35	82	Sand
8C	202–215	466	499	7	26	10	38	Sand

AD Clay dispersed in water, *GD* degree of dispersion, **3C* slag gravelly material

(Bomfim et al. 2015). Once the toxic elements reach the soil, they can be adsorbed by soil particles, transported superficially, absorbed by plants, or leached. The physical and chemical characteristics of soil, topography, and the solubility of metals determine the prevailing mechanism.

The deposition of particulate materials [60% Pb, 10% Zn, 6% Cd, and 5% Fe; Oliveira (1977)] from factory chimney was one of the main routes of air, water, and soil contamination, thus resulting in high Pb concentrations in the profiles P1 to P4. In the profile P5, small piles of slag were observed. In the profiles near the plant (P1

and P2), the metal concentrations varied from 1387.9 to 857.8 mg kg^{-1} for Pb, from 6.0 to 1.0 mg kg^{-1} for Cd, and from 127.9 to 72.8 mg kg^{-1} for Zn in the horizons Ap1 and Ap of P1 and P2, respectively. Pb and Cd tended to accumulate superficially in P1 and P2; however, their concentrations decreased along the profile. The high concentrations of Pb and Zn at the soil surface were associated with the atmospheric deposition of particulates from the factory chimney, whereas the presence of these metals in different layers can be attributed to the movement of soils between horizons. The process of pedoturbation was

Table 3 Chemical characteristics of the soil profiles sampled in toposequence that extends from the vicinity of the old lead factory to the banks of the Subaé River, Santo Amaro, Bahia

Layer	Depth	pH		Δ pH	C. org.	Ca^{2+}	Mg^{2+}	Na^{+1}	K^{+1}	Al^{3+}	H + Al	SB	CEC	Targila	m	V
	cm	H_2O	KCl		dag kg^{-1}	cmol$_c$ kg^{-1}									%	
Profile 1																
Ap1	0–5	6.0	4.8	− 1.2	0.5	27.5	19.5	0.1	0.5	0.3	9.6	47.6	57.2	112	0.6	83
Ap2	5–15	5.2	3.7	− 1.5	0.3	24.5	10.9	0.1	0.4	0.6	12.9	36.0	48.8	80	1.6	74
AB	15–39	5.3	3.8	− 1.5	0.2	25.5	8.5	0.2	0.3	0.7	10.7	34.4	45.2	71	2.0	76
BA	39–47 (46–49)	5.3	3.8	− 1.5	0.1	25.5	7.8	0.3	0.3	1.0	8.9	33.9	42.8	62	2.9	79
Biv	47–63 (56–70)	4.9	3.6	− 1.4	0.1	27.5	10.1	0.3	0.3	3.5	11.4	38.2	49.6	68	8.4	77
C	63–85+	6.4	4.3	− 2.1	0.1	39.5	12.0	0.3	0.3	0.3	3.0	52.1	55.1	83	0.6	95
Profile 2																
Ap	0–7	6.1	4.8	− 1.3	0.3	33.0	11.5	0.1	0.4	0.3	6.9	45.0	52.0	79	0.7	87
AB	7–28 (20–37)	6.6	4.1	− 2.6	0.1	38.6	11.4	0.1	0.3	0.4	8.1	50.4	58.5	85	0.8	86
Biv	28–48 (46–53)	6.0	4.1	− 1.9	0.1	40.7	3.9	0.2	0.3	0.5	6.3	45.2	51.4	78	1.1	88
BCv	48–55 (53/57)	6.3	4.3	− 2.0	0.1	37.5	8.5	0.2	0.4	0.3	4.8	46.6	51.4	83	0.6	91
C	55+	8.4	6.5	− 1.9	0.0	40.6	9.0	0.2	0.1	0.3	1.0	49.9	50.9	88	0.6	98
Profile 3																
Ap	0–5	8.1	6.7	− 1.4	0.2	28.5	3.5	0.1	0.2	0.1	0.5	32.3	32.8	63	0.3	99
C1	5–35 (25–40)	8.3	6.8	− 1.5	0.0	28.0	4.0	0.1	0.1	0.1	0.3	32.1	32.4	64	0.3	99
C2	35–78	8.3	6.9	− 1.4	0.1	23.5	8.0	0.1	0.1	0.1	0.5	31.7	32.2	69	0.3	98
C3	78–100	8.5	8.1	− 0.4	0.2	2.5	3.0	0.1	0.1	0.1	1.2	5.7	6.8	–	1.7	83

commonly observed in the vertic horizons because of the expansion and contraction of clay, and consequently, the formation of cracks along the profiles facilitated the redistribution of metals.

The concentrations of Pb in P1 and P2 were above and around the industrial intervention value, respectively, whereas Cd concentration was above the agricultural intervention value in P1 and about the prevention value in P2. According to the Brazilian Environmental Agency (CONAMA 2013), Zn concentrations in both P1 and P2 were between reference quality and prevention value (Table 4).

Soil samples collected in the middle third (P3) and the lower third of slope (P4) possessed highest concentrations of Pb, Cd, and Zn (Table 4). The highest Pb concentration (23,713.4 mg kg^{-1}) was found in the layer 3C of P3. Zn concentrations in P3 ranged from 236.9 mg kg^{-1} (in 2C) to 1858.9 mg kg^{-1} (in 3C). However, Cd did not follow the same pattern as Pb and Zn, higher Cd concentrations were detected in the top soil, and the concentration started to decrease with depth because of its mobility in soils.

The concentrations of Pb were above the industrial intervention level in the horizon and the layers of P3 excepting the layer C1, where Pb concentration was between residential and industrial concentrations (Table 4). Cd concentration was about or above the industrial intervention concentration. The Zn concentration of layer 2C-P3 was in the industrial range; in Ap and C1, the concentration was between agricultural and residential intervention; and in the layer 3C, it was between residential and industrial concentrations (Table 4).

Pb concentrations in first two horizons of P4 (4498.9 mg kg^{-1} for Ap and 2136.0 mg kg^{-1} for ABv) were above the industrial intervention range (CONAMA 2013). Cd concentrations in Ap and ABv horizons of P4 were at or above the threshold of industrial intervention value (CONAMA 2013) (Table 4). Zn concentrations in the top 28 cm of P4 (348.9 mg kg^{-1} for Ap and 325.4 mg kg^{-1} for ABv) were above the prevention value.

The Pb concentration in the top 28 cm of P4 was highest among all profiles, whereas Cd and Zn concentrations in the same horizon of P4 were lower than that in P3 (Table 4). Moreover, high concentrations of metals were found in P4 (a profile located outside the perimeter of the plant) it can be attributed to the transference of soil and sediments from P3 to P4.

The Pb concentration of layer 4C was between agricultural and residential values, whereas the concentrations of Pb and Zn in P5, the profile farthest from the contamination site and closest to Subaé River, were the lowest among all profiles. The results indicate that the contaminants are moving toward the river. The high metal concentration was found in the soils located outside the plant boundary (P4 and P5); this finding was in full agreement with the results of Asevedo (2012) and

Table 4 Heavy metal concentrations of the soil profiles near the old lead factory, on the banks of the Subaé River, Santo Amaro, Bahia

Layer	Depth	Pb	Cd	Zn
	cm	mg kg^{-1}		
Profile 1				
Ap1	0–5	1387.9	6.0	127.9
Ap2	5–15	578.1	LD	44.35
AB	15–39	510.7	LD	78.59
BA	39–47 (46–49)	422.7	LD	109.85
Biv	47–63 (56–70)	427.9	LD	53.48
C	63–85+	428.3	LD	0.13
Profile 2				
Ap	0–7	857.8	1.0	72.8
AB	7–28 (20–37)	531.04	LD	50.57
Biv	28–48 (46–53)	421.58	LD	25.48
BC	48–55 (53/57)	420.99	LD	79.99
C	55 +	341.39	LD	81.86
Profile 3				
Ap	0–5	1496.32	51.30	536.69
C1	5–35 (25–40)	645.71	19.74	679.15
2C	35–78	4068.17	17.64	236.9
3C	78–100	23,713.4	29.05	1858.9
Profile 4				
Ap	0–12	4498.9	20.76	348.9
ABv	12–28	2136.0	18.07	325.4
BAv	28–40	*LD	0.10	83.30
Biv	40–71	LD	LD	51.63
C	71–95	LD	LD	55.90
Profile 5				
A	0–10	289.59	LD	39.16
C	10–43 (34–39)	251.80	LD	41.90
2C	43–76 (72–80)	227.59	LD	17.07
3C	76–96 (90–107)	216.65	LD	31.74
4C	96–132	193.65	LD	16.14
5C	132–149	LD	LD	35.27
6C	149–166	LD	LD	18.51
7C	166–202	LD	LD	18.45
8C	202–215	LD	LD	7.55
CONAMA (2009)	Pb mg kg^{-1}		Cd mg kg^{-1}	Zn mg kg^{-1}
Quality reference	17		<0.5	60
Prevention	72		1.3	300
Agricultural intervention	180		3.0	450
Residential intervention	300		8.0	1000
Industrial intervention	900		20	2000

*LD Detection limit of the atomic absorption apparatus

Bomfim et al. (2015). Moreover, the presence of Pb on the surface horizon of the flat lowland soil region (P5) indicates that after two decades of inactivity of the plant, the transference of contaminated materials still continues to occur from the contaminated site toward the river and estuary due to the erosion of soil.

Cd concentration was below the detection limit for all profiles, and Zn concentration was in the range of reference quality value (CONAMA 2013). The low concentrations of

Table 5 Classification of the soils of the toposequence according to the World Reference Base for Soil Resources (IUSS Working Group WRB 2015) and the Brazilian System of soil Classification (SIBCS), Santos et al. (2013)

Profiles	System of Soil Classification	
	IUSS Working Group WRB (2015)	SIBCS (Santos et al. 2013)
1	Pellic Vertisol (Hypereutric, Anthrotoxic)	Vertissolo Háplico Órtico típico
2	Leptic Vertisol (Hypereutric, Skeletic, Anthrotoxic)	Vertissolo Háplico Órtico típico
3	Leptic Endospolic Technosol (Eutric, Clayic, Hyper-artefactic, Orthoskeletic, Anthrotoxic, Transportic, Protovertic)	Neossolo Regolítico Eutrófico típico
4	Haplic Vertisol (Hypereutric, Gleyic, Anthrotoxic)	Vertissolo Háplico Órtico gleissólico
5	Eutric Fluvisol (Loamic, Phytotoxic)	Neossolo Flúvico Ta Eutrófico típico

Pb, Zn, and Cd in P5 were due to the low content of key parameters related to metal retention.

Classes of soils

The soils of the toposequence were classified according to the World Reference Base for Soil Resources (IUSS Working Group WRB 2015) and the Brazilian System of Soil Classification (SIBCS) (Santos et al. 2013) (Table 5). In the WRB system, the attributes related to natural or anthropogenic contaminants are in the second level; however, in SiBCS, they are described in the fifth level.

According to the IUSS Working Group WRB (2015) system, the prefix *Toxic* was used for second-level units to indicate the presence of toxic concentrations of organic or inorganic substances (other than the ions Al, Fe, Na, Ca, and Mg) in any layer within 50 cm of the soil surface and the term *technic* was used for higher categorical level, for soils with the formation similar to the observed in P3.

According to the 4th categorical level (maximum level of structure in SiBCS) of the Brazilian System of Classification (Santos et al. 2013), the terms contaminated and anthropic were included in the fifth category level and the sixth category level of P5, respectively, in order to indicate the human influence on soil formation.

Conclusion

The soils of the toposequence were classified into five categories: Pellic Vertisol (Hypereutric, Anthrotoxic—P1), Leptic Vertisol (Hypereutric, Skeletic, Anthrotoxic—P2), Leptic Endospolic Technosol (Eutric, Clayic, Hyperartefactic, Orthoskeletic, Anthrotoxic, Transportic, Protovertic—P3), Haplic Vertisol (Hypereutric, Gleyic, Anthrotoxic–P4), and Eutric Fluvisol (Loamic, Phytotoxic–P5). The high clay dispersion index ($> 63\%$) and the predominant wavy relief made the soils highly susceptible to erosion. The contaminants and slag from the lead alloy processing industry were disposed of in the P3 region, thus causing an increase in Pb concentration ($> 2\%$). The accumulation of metals in the Haplic Vertisol (P4) and the Eutric Fluvisol (P5) regions evidences that the transference of contaminants still continues to occur from the top to the lowland area of the toposequence after two decades of incorrect disposal of mine tailing materials.

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